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Description of hydrogen storage in hydrides and related compounds by quantum chemical calculations

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ABSTRACT:

An understanding of the process of storing hydrogen as hydrides in various metal or more complex lattice structures can be obtained on the basis of quantum chemical potential energy studies. The calculations aim at identifying interesting compounds for further study, rather than embarking on trial and error experimental perusal of large numbers of potential structures. The method is gaining confidence by study of simple compounds, such as MgH_2, with known hydrogen storage properties [1]. The present communication updates this work on MgH_2 with a discussion of thermodynamic properties and swelling caused by the absorption of hydrogen, and embarks on a study of the considerably more complex case of $LaNi_5H_x$, where experimental work finds hydrogen present with $6 < x < 7$. It is found from simple quantum point calculations, that hydrogen will gain energy by spontaneous absorption in this structure, and that $x=6$ energetically is slightly favoured over $x=7$.

KEYWORDS : *Metal hydride storage, quantum chemistry, thermodynamics, potential energy.*

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1. Introduction

Two avenues have been explored for the modelling of hydrogen storage in metals or metal compounds. One is to use point calculations with Gaussian bases to explore density functional theory descriptions for individual hydrogen atoms stored in a small chunk of the metal lattice. The second method uses fast Fourier methods to solve the equations for the case of periodic boundary conditions, allowing considerably larger sizes of lattices to be handled in a short time [2]. However, in order to fulfil the conditions for periodicity of boundary conditions, all hydrogen atoms must be moved in and out of the metal lattice in unison, as illustrated in Figure 1.

Metal hydrides offer hydrogen storage at near-ambient pressures (0.06-6 MPa), with high round-trip efficiencies and with high safety in operation. Hydrogen transfer is accomplished by adding or withdrawing modest amounts of heat, a process that often takes hours but in a few cases can be carried out on a time-scale of a few minutes, as required for most automotive applications. In the case of MgH_2, a promising binary metal hydride, the methods mentioned above explain the observed energy gain, obtained by absorption of hydrogen, when moved into the equilibrium position inside the lattice [1]. Similar calculations also confirm the inability of other metal lattices, such as that of nickel, to gain

energy by hydrogen absorption. The section 2 below adds new calculations aimed to investigate the swelling of the lattice upon absorbing hydrogen.

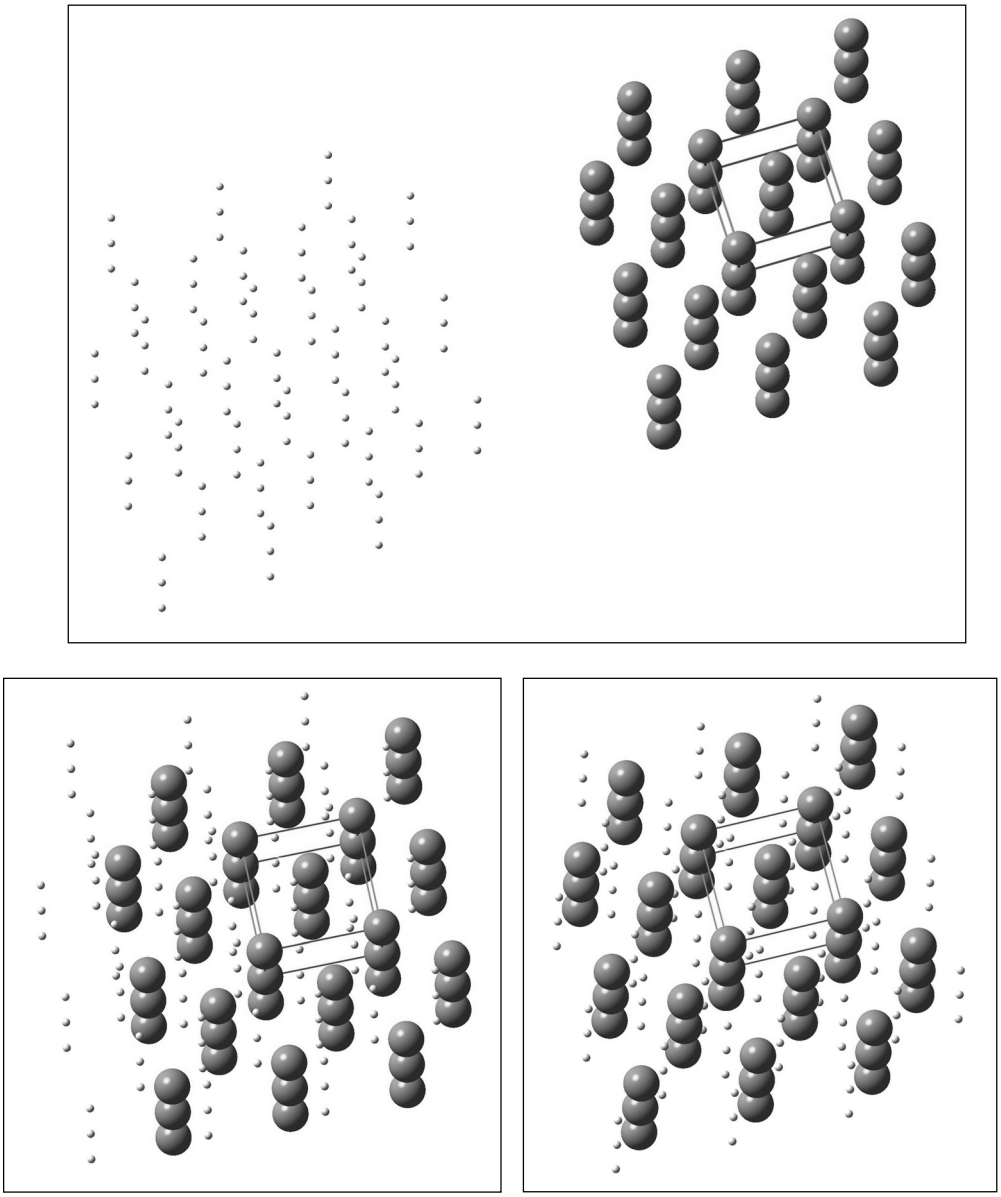

Figure 1. Three stages depicting the absorption in unison of hydrogen into a magnesium lattice, as modelled with periodic boundary conditions. A unit cell is indicated.

Another compound which has attracted interest because of its high volume hydrogen density is $LaNi_5H_x$, with x= 6 to 7 The ternary structure of this hydride has been shown to lead to very asymmetrical equilibrium positions of H-atoms within the lattice, as determined by calculation by several authors using density functional theory with limited optimisation procedures [3, 4]. Experimentally, there

is a tendency for less than 7 hydrogen atoms to enter each unit cell, which has been attributed to a distortion of the lattice caused by previously absorbed hydrogen. New calculations are presented here in section 3 for the change in potential energy for different numbers of hydrogen atoms entering the lattice.

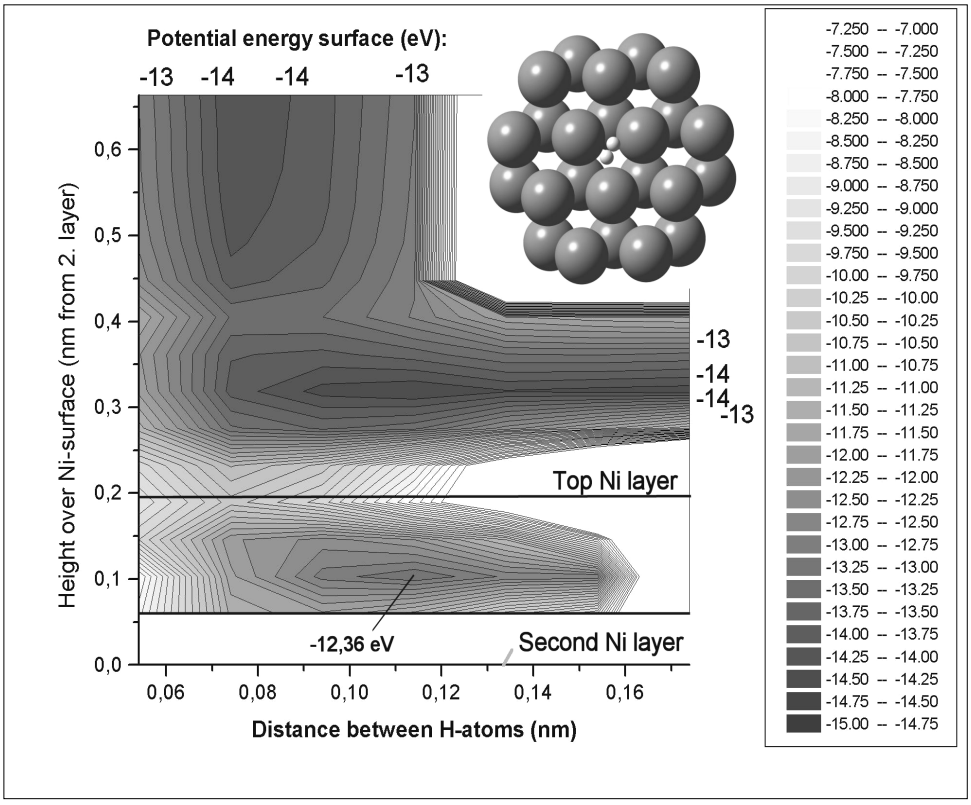

Figure 2. Potential energy surface in eV for two hydrogen atoms near (above or under) a nickel surface: the variational coordinates are distance between hydrogen atoms and height of the center of mass of the two H atoms over the (1,1,1) surface of the Ni-layer below the top layer. The energy scale has an arbitrarily chosen origin [1}.

2. Magnesium hydrides

Among single-metal hydrides, MgH_2 with a hydrogen fraction of 7.6% by mass is of interest, despite the fairly high desorption temperature of about 330°C. The enthalpy of formation for the binary hydride at this temperature is –74.5 kJ mol^{-1} and quantum chemical calculations have been used to study the swelling of the metal lattice when incorporating hydrogen [5,6]. That suitability for hydrogen storage is not granted all metals is illustrated by the potential energy surface for two hydrogen atoms near a nickel surface illustrated by the extended potential energy surface shown in Figure 2. It is calculated using the B3LYP parametrisation of the density functional method [7]. The dissociation of the hydrogen molecule into two atoms takes place outside the Ni surface, as reproduced by previous calculations [1,8]. An additional potential energy minimum is found within the Ni surface, midway between the first two layers, but a quite high barrier (about 4 eV) has to be tunneled through for the H-atom to get there, and the minimum is some 2 eV higher than that of separated H-atoms outside the surface, so that spontaneous transfer is not encouraged except for a tail of the thermal distribution. In

the following, I look at hydrogen near an Mg surface, in order to see if the calculated conditions are more favorable for group-II metals.

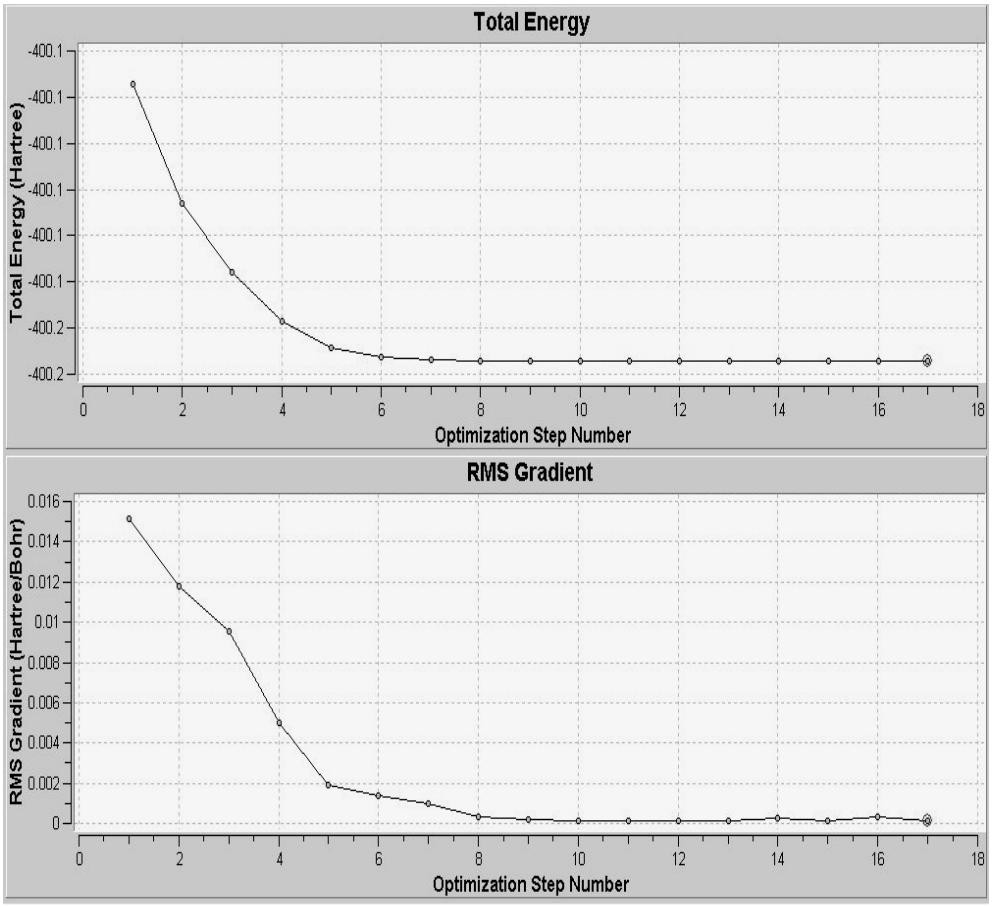

Figure 3. Stepwise approach to optimised structure of MgH_2, based on calculations using density functional theory. The upper graph shows the diminishing of total energy, and the lower one the maximum gradient found at each step, for each point calculation step.

The calculation for MgH_2 is carried out using density functional theory with periodic boundary conditions and fast multipole techniques [2,9,10], rather than explicitly treating the periodic lattice as a single large molecule similar to the calculation for NiH in Figure 2. In this way, the computing time is reduced by nearly two orders of magnitude. The SV basis set [11] is used with automatic optimisation, as implemented in the Gaussian software package [12], and the PBEPBE parametrisation is used for the density functional exchange and correlation parts [13]. The periodicity is allowed to prevail for about 1.6 nm in directions along the Mg-surface and into the material, which was verified to be enough to ensure stability of calculated energies.

The structure of MgH_2 is first subjected to optimisation, with H atoms occupying the positions within the lattice leading to minimum potential energy. As shown in Figure 3, the approach to the minimum energy state is very rapid. In order to compare the energy of this system to those of the same system but with hydrogen atoms partially or fully outside the Mg lattice, a sequence of calculations were made, pulling the hydrogen atoms out of the lattice but preserving their relative positions among

themselves, as indicated in Figure 1. This allows the periodic boundary condition method to be used throughout. Figure 4 shows the potential energy curve along the center-line of displacement. All potential energies are given per unit cell of two Mg-atoms and four H-atoms, with arbitrary but identical origin for all displacement calculations. The enthalpy of formation is calculated from a frequency analysis and is found to be -72 kJ/mol at standard temperature (298 K) and pressure (101 kPa), in good agreement with the experimental value of –74.5 kJ/mol [15] obtained at the temperature 330 K.

The swelling of the lattice is investigated by optimising the structure with and without hydrogen atoms absorbed. The Mg-Mg distance in the above-mentioned optimised MgH_2 lattice is d = 0.331 nm. Repeating the optimisation using periodic boundary conditions, still with the same density functional theory-parametrisation and set of basis functions, for a lattice, where the hydrogen atoms are pulled halfway out (0.4 nm), one finds that the Mg-Mg distance is changed by 0.004 nm. The swelling occurring from a situation with no hydrogen atoms to two per Mg atom is thus 1-2%

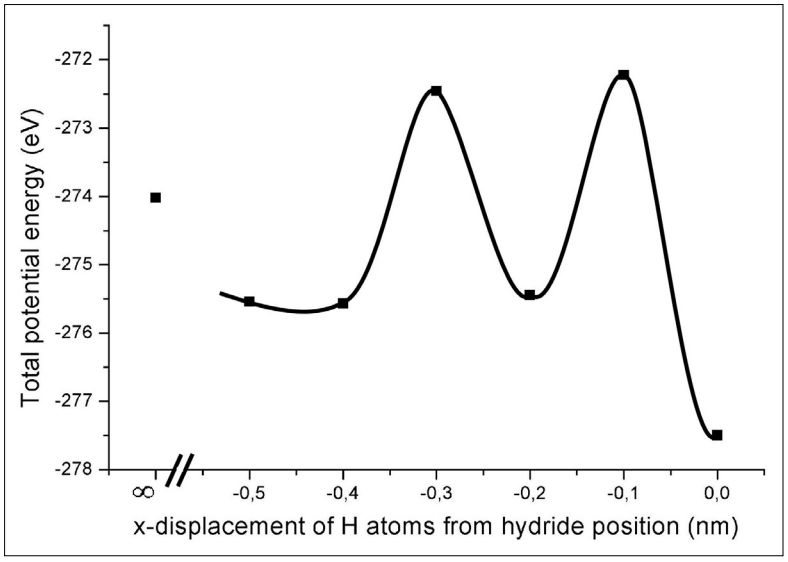

Figure 4. Potential energy plot for Mg-2H system as a function of displacement perpendicular to the lattice surface [1}.

3. $LaNi_5H_x$: A binary metal hydride

Among the hydrides with two metal constituents, $LaNi_5H_x$ with x = 6 or 7 has attracted attention due to its high hydrogen content by volume (115 kg per m^3 for x=6). Its gravimetric hydrogen density is low (mass percentage around 2) and the enthalpy evolution during absorption –30 kJ/mol [14]. Various guesses regarding the molecular structure of $LaNi_5H_6$ and $LaNi_5H_7$ have been subjected to quantum calculations using density functional theory but often a small number of unit cells [3,4]. Figure 5 shows the proposed structure of $LaNi_5H_7$. The very unsymmetric location of the hydrogen atoms indicates the influence of long-distance Coulomb forces reflecting the different effective charges of nickel and lanthanium atoms. There is no simple path for collectively bringing hydrogen atoms from the exterior to the inside of the lattice in the way adopted for the MgH_2 molecule shown in Figure 1. Therefore, the periodic boundary condition type of calculation is not considered appropriate in this case. Furthermore, several of the well-tested basis sets used in density functional theory are not available for La, so quantum chemical calculations are bound to be more difficult or uncertain.

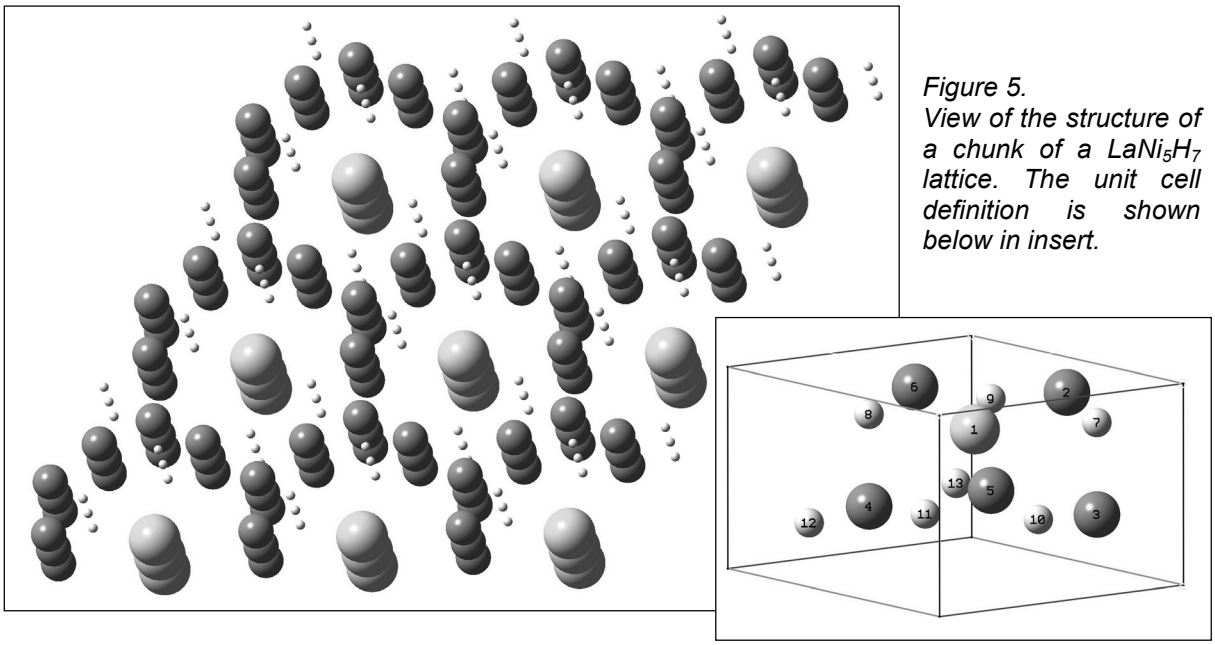

Figure 5.
View of the structure of a chunk of a $LaNi_5H_7$ lattice. The unit cell definition is shown below in insert.

The experimental observation of often less than 7 hydrogen atoms absorbed may be associated with the swelling of the parts of the lattice having already absorbed 7 H atoms per unit cell, making it less likely for the remaining ones to accommodate more than 6 H atoms. Figure 6 indicates the position of a hydrogen atom more squeezed between the larger atoms of the two unit cells shown and thus a probable candidate for the sometimes missing H-location. As it will be shown below, such explanations turn out not to be required for understanding the less than maximum filling with absorbed H atoms. Both the present and the previously published calculations rule out accommodation of more than 7 H atoms in the structure.

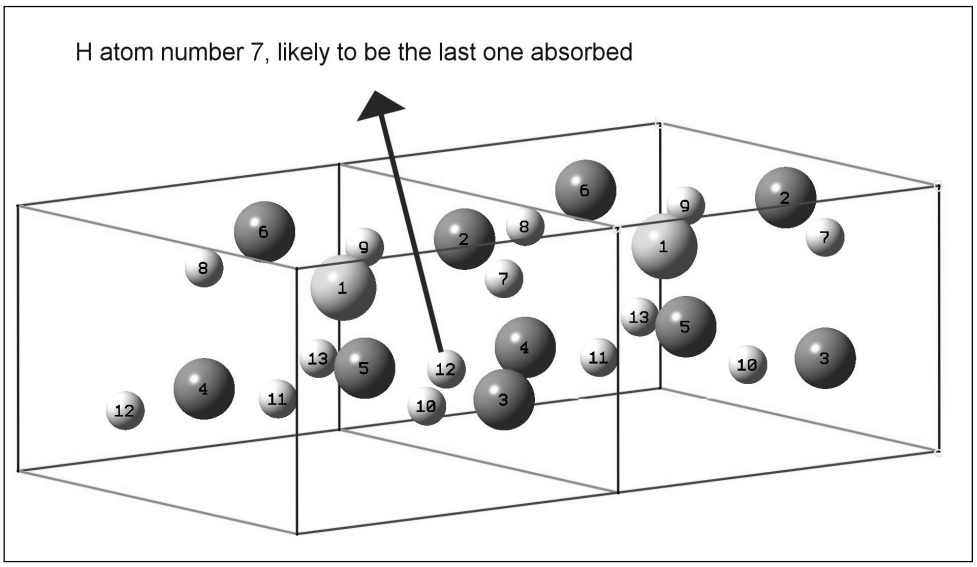

Figure 6.
Two unit cells of $LaNi_5H_7$, indicating the H atom position likely to be the last to be filled.

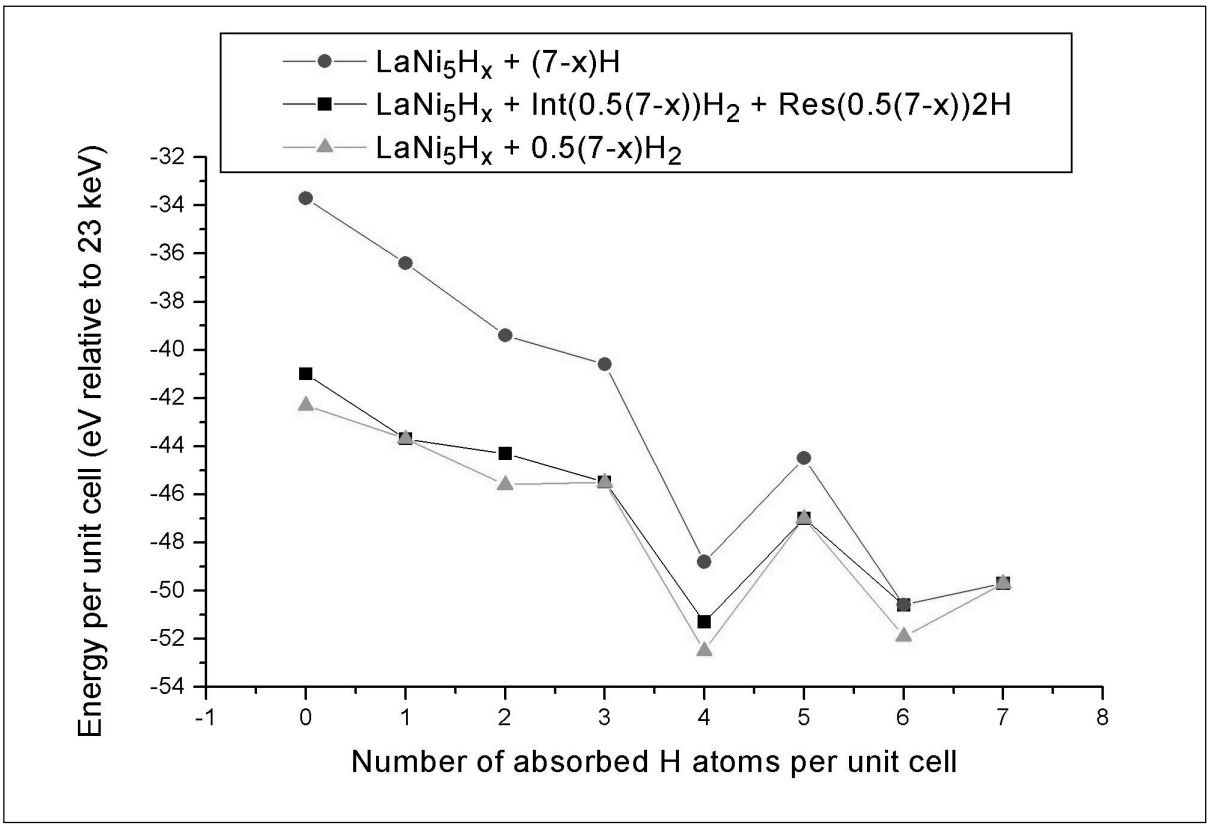

Figure 7. Total energy per unit cell for $LaNi_5$ plus 7H, with different number of hydrogen atoms x absorbed into the lattice. For the upper curve, the energy of external hydrogen atoms is added as that of free atoms, while in the lower two curves, they are assumed to form molecular H_2 outside the lattice. This again comes in two variants, either with half of the molecular energy per external atom, or staggered according to whether the number of outside H's is even or odd (and in the latter case using the free H energy for the last atom rather than half the molecular energy).

Figure 7 shows the results of a series of one-cell Hartree-Fock point calculations with the basis set CEP-31G taken from [16]. There are 218 symmetry-adapted basis functions for the 54 electrons per unit cell, and for x<7, the hydrogen molecular energy is calculated using the same basis and the standard distance between H atoms. Repeating the calculations with density function theory of the parametrisation PBEPBE [13] changes energies by less than 1%.

First of all, the calculation presented in Figure 7 shows that hydrogen molecules are indeed spontaneously penetrating into the $LaNi_5$ lattice and forming hydrides at ambient temperature and pressure. The energy drop for the first 4 hydrogen atoms is quite large and suggests a rapid process of filling. However, the behavior for the remaining hydrogen atoms is oscillatory, although only by a few eV, suggesting that thermal distributions of velocities will be sufficient to complete the absorption, albeit with longer periods of time required. In all three versions of the curve given in the figure, there is a slight rise in energy for the seventh hydrogen atom seeking an interstitial depository. This in itself would explain the experimental finding of between 6 and 7 atoms spontaneously absorbed per unit cell. However, the particularly dip in the energy surface for the 4^{th} H atom may offer the alternative

explanation of a broader distribution of 4-7 hydrogen atoms per unit cell, still without involving the swelling in the argument. However, all these mechanism could be at play and consistent with experiments, which are currently unable to determine the structure inside each unit cell.

3. Concluding remarks

The question asked at the outset, of whether theoretical quantum calculations could be used to assess hydride properties, has been answered in the affirmative. However, the further question, if theoretical explorations can replace experimental trial and error efforts, is more difficult to answer. Maybe to some extent, but the time saved may be minimal, because the theoretical calculations are often not so simple to carry through as one may first think: Before a given molecule can be discussed, it is often necessary to run a large number of quantum calculations, in order to find the best model parameters, to avoid numerical instabilities and to ensure that the requested accuracy is sufficient. Furthermore, for the larger molecules, a trade-off between accuracy and computing time has to be found, not to mention refraining from calculations exceeding computer memory capacity or real time available. In those cases where the fast Fourier methods available in cases of periodic boundary conditions are not valid, calculations may require several months of CPU time on state-of-the-art computers, because many unit cells have to be included if realistic modeling of the pathways of intruding hydrogen molecules through the lattice is to be made.

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